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Dissociative Recombination

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ABSTRACT

We consider the following process. A hydrogen molecular ion H_2^+ in its ground state, $(1s\sigma_g)\ {}^2\Sigma_g^+$ captures a free electron of low energy, and splits up into two hydrogen atoms. For low energy of the incident electron, the resulting hydrogen atoms will carry off most of the binding energy of the molecular ion as electronic energy of excitation rather than as relative kinetic energy of the nuclei. Two important final states of the atoms are (1s, 2s) and (1s, 2px). The cross section for transitions into these two states are calculated as a function of electron energy for energies less than 1 ev, and are found to be of gas kinetic order of magnitude (10^{-15} cm^2).

1. Introduction

We wish to calculate the cross section for the following process:

$$(1) \qquad X_2^+ + e \longrightarrow X_2^* \longrightarrow X + X' ,$$

where X is any "reasonable" molecular species. The reaction (1) with X = oxygen seems to be important in the upper atmosphere[1]; the reaction (1) with helium has been examined experimentally by Biondi and Holstein[2]. In the following we shall restrict ourselves to the case of hydrogen, as this can be calculated with comparatively little labor and displays most of the features to be expected in more complicated atoms.

In the process (1) an electron e of kinetic energy $\hbar^2 k^2/2m$ relative to the center of mass of a positive molecular ion X_2^+ combines with the ion in a process of charge neutralization. There results an excited molecule X_2^* which may dissociate into two atoms; normally at least one of these atoms will have electronic energy of excitation.

A detailed investigation of the conservation requirements is given in Appendix A where we find that the molecule X_2^* must have some internal energy of excitation but need not be unstable. However, the case we are particularly interested in here is that where X_2^* does break up into two atoms. We study this particular case because we expect it to be rather probable, as it involves a transition between two states in a continuous spectrum, rather than a transition from a continuous to a discrete state which would be involved if X_2^* were a stable but electronically excited state.

We may carry out one of two calculations which look rather different but which should be equivalent:

a) Consider the X-nuclei at rest at a fixed nuclear separation R_k, and calculate the capture cross section for the process

$$X_2{}^+ + e \longrightarrow X_2^* \quad (R = R_k) , \tag{2}$$

where X_2^* is in some state which breaks up into $X + X'$ asymptotically as $R \to \infty$.

Conservation of energy imposes the following condition:

$$E_{X_2{}^+}{}^{e\ell}(R_k) + \hbar^2 k^2/2m = E_{X_2{}^*}{}^{e\ell}(R_k) , \tag{3}$$

which gives the nuclear separation R_k at which the reaction (2) occurs as a function of k. $E_P{}^{e\ell}(R)$ denotes the electronic energy of the system P at a nuclear separation R.

The actual appearance of the situation of Eq. (3) is shown in Fig. 1 for two possible states X_2^*, X_2^{**}, in the case X = hydrogen. The H_2^+ ion in its ground state $(1s\sigma_g)^2\ {}^{}\Sigma_g^+$ has a much greater energy asymptotically (13.5 ev) than has the H_2 molecule in its lowest reasonable state, namely[†] $(1s\sigma_g)(2p\sigma_u)\ {}^3\Sigma_u$. It follows from this that the potential energy curves of these two states only cross for R considerably smaller than the equilibrium nuclear separation of the ion, R_I. Thus the probability of finding the ion at a suitable nuclear separation R_k is very small, and hence so is the reaction probability.

Let us now consider the case when asymptotically our system is H(1s) + H(2s or 2p...), so that H_2 is taken as H_2^* (1sσ or 2pσ) (2sσ or 2pπ). In this case the asymptotic energy difference between H_2^+ and H_2^* will be $\frac{1}{4} \times 13{,}6 = 3.4$ ev, so that the potential energy curves may cross at a value of R much closer to R_I than for the case H_2(1sσ) (2pσ), making possible much larger reaction cross sections. This result is not really very surprising. It seems plausible that the end products of "chemical" and other such processes are generally found in excited states; presumably such processes provide the principal mechanism for producing excited atoms. In particular, one would imagine that this general behavior should be found in molecular species X other than hydrogen.

[†] Note that both the (1sσ) and the 2pσ) states lead asymptotically to a (1s) state.

Potential energy curves for various electronic states of the hydrogen molecular ion H_2^+ and of the molecule H_2, as a function of nuclear separation R. The energies of t the molecular states are derived from the eigenvalues of ionic states, but with the nucleus-nucleus Coulomb repulsion counted only once. This is necessary for consistency cf. Section 2. We consider transitions from H_2^+ $1s\sigma_g^2\ \Sigma_g^+$ into $H_2(Bg)$ or $H_2\left\{(2p\sigma_u)(2s\sigma_g) \equiv Cu\right\}$ by capture of a free electron. The Bg and Cu states have practically the same energy.

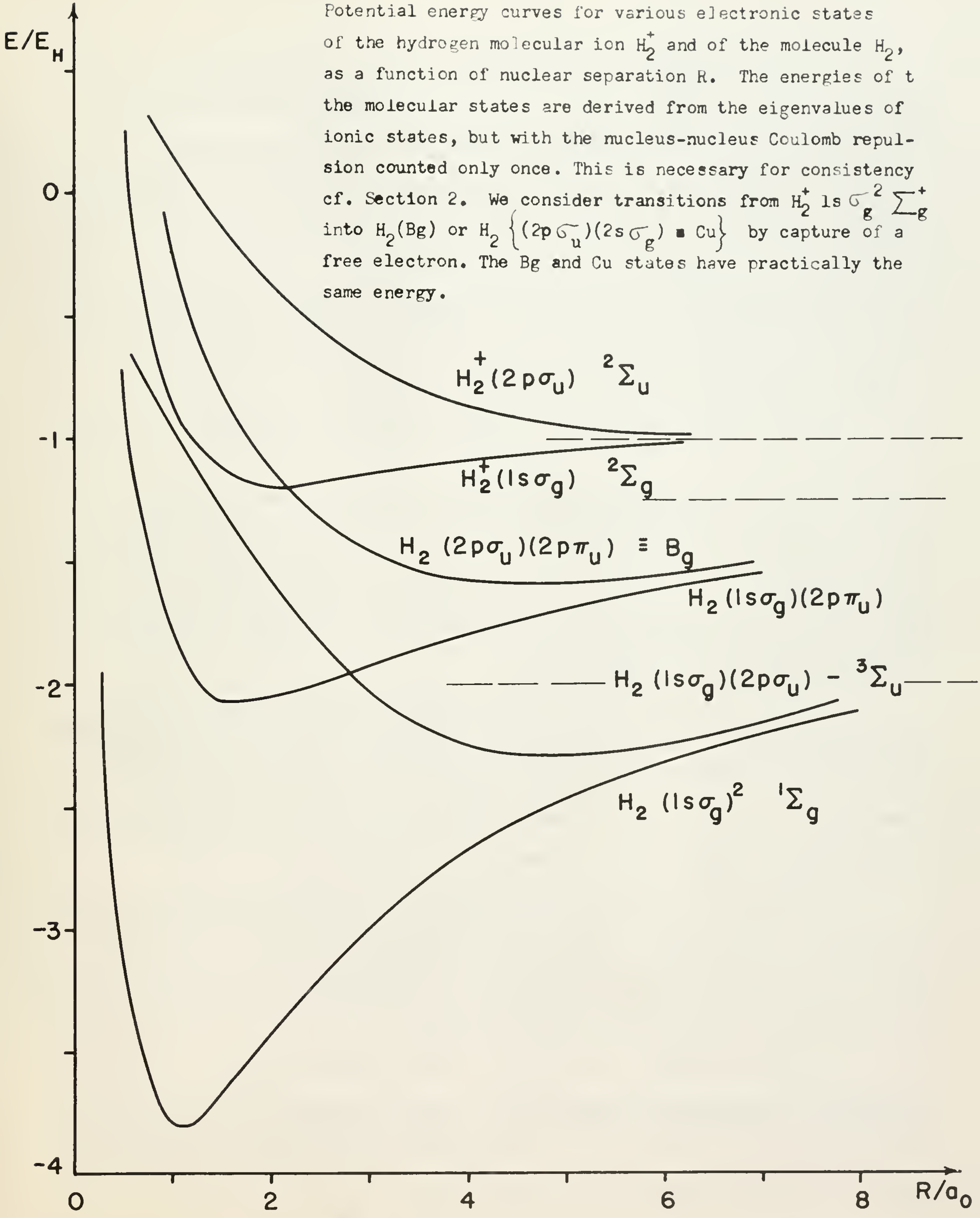

Figure 1

In the following discussion we shall only consider the method a); but the other possible method of attack will now be outlined.

b) If we do not consider the X-nuclei to be at rest but permit them to move, treating the nuclear coordinate R as a dynamical variable, then we have to calculate the cross section for the process

$$(4) \qquad X_2^+ + e \longrightarrow X + X' ,$$

in which the nuclei X,X' fly apart with relative velocity $\hbar K/M$. The condition of conservation of energy now becomes

$$(5) \qquad E_{X_2^+}^{e\ell}(R_1) + \hbar^2 k^2/2m + \tfrac{1}{2}\hbar\omega_I = E_X^{e\ell}(R_2) + E_{X'}^{e\ell}(R_2) + \hbar^2 K^2/2M.$$

$E^{e\ell}$ again refers to the electronic energy of the appropriate state at the value given for the nuclear separation; thus $R_1 = R_I$ the equilibrium nuclear separation of the ion while $R_2 = \infty$. Note that the zero-point vibrational energy of the ion, $\frac{1}{2}\hbar\omega_I$, enters here; it cannot occur properly in the case a), where the nuclear coordinate is merely a classical parameter.

Thus, what happens here is that an amount $(\hbar^2 K^2/2M - \frac{1}{2}\hbar\omega_I)$ of energy is transferred from the electronic to the nuclear motion. This is "well known"[3] to be improbable except for very small energies, so that again one sees that the state H(1s) + H(2s, or 2p) is much more probable to result from the collision than the state H(1s) + H(1s) .

There seem to be considerable difficulties in attempting the calculation b), and thus for the present we shall restrict ourselves to a); but one feels certain that both methods must be equivalent, i.e., must give the same result for the same initial $(X_2^+ + e)$ and final $(X_2^* \rightarrow X + X')$ states.

In the calculation that follows we shall restrict ourselves to the case of hydrogen, as has been said already, and we shall only consider slow electrons, with $\hbar^2 k^2/2m \lesssim 1$ ev, that is, $ka_0 < 1$. Thus we shall expand the cross section in powers of k, retaining only the lowest-order terms.

2. Outline of the calculation

Consider two protons A, B and two electrons 1,2. Initially one electron is free, and the other in the lowest ($1s\sigma_g\ {}^2\Sigma_g$) state of the molecular ion H_2^+. During the electronic transition under consideration here, the nuclear separation $R = AB$ remains constant; the final state of the system corresponds to an unstable excited molecule H_2^*, which will automatically split up into one normal (1s) hydrogen atom, and one excited atom (2s, or 2p...) .

To carry out a perturbation calculation, we have to specify the unperturbed hamiltonian H_o:

(6) $$H_o = -(\hbar^2/2m)(\nabla_1^2 + \nabla_2^2) - e^2(1/r_{1A} + 1/r_{1B} + 1/r_{2A} + 1/r_{2B}) + e^2/R ,$$

and the perturbation V' :

(7) $$V' = e^2/r_{12} .$$

Thus, we treat the interaction of the electrons with the nuclei, and also the nucleus-nucleus coulomb repulsion, e^2/R, as part of the unperturbed hamiltonian, and consider the electron-electron coulomb repulsion as the perturbation inducing transitions. It follows from this separation that if we wish to build up our wave functions from one-electron functions, then we must use ionic one-electron functions - i.e., eigenfunctions of H_2^+ rather than of H_2 .

Next, we construct the potential energy curves of Fig. 1 for various states, because in this way we can decide which transitions are likely to have reasonably large transition probabilities. The initial state is clear: the H_2^+ ion has two states whose asymptotic form (for infinite nuclear separation) is $H^+ + H(1s)$, namely the stable ground state $1s\sigma_g$, and the unstable state* $2p\sigma_u\ {}^2\Sigma_u$.

---

* The potential energy curves for both of these states, and all others in Figs.1,2, are taken from E. Teller[4] cf.[5], p.203 ff.

The final state will be a combination of two one-electron H_2^+ eigenstates, with the nucleus-nucleus coulomb repulsion counted only once; we require states whose asymptotic form is $H(1s) + H(2s,2p\ldots)$. One thing that is immediately obvious is that of the two ionic states that give $H(1s)$ asymptotically, only H_2^+ $2p\sigma_u$ is possible, because no combination of a bound ionic state with the H_2^+ $1s\sigma_g$ state can possibly give a potential energy curve that crosses the H_2^+ $1s\sigma_g$ ${}^2\Sigma_g$ energy for any finite R.*

We find that the states $2s\sigma_g$, $2p\pi_u$ are very similar in energy, and the combinations $H_2(2p\sigma_u\, ,\, 2s\sigma_g\, {}^{1,3}\Sigma_u)$ and $H_2\ (2p\sigma_u,\, 2p\pi_u\ {}^{1,3}\Pi_g)$ offer possible final states H_2^* of Fig. 1; in fact these states, which are the lowest lying states above $H_2(1s\sigma_g,\, 2p\sigma_u\ {}^3\Sigma_u)$ will be considered. There seems no particular reason to suppose that higher states of type $(2p\sigma_u,\, 3s,p,d\ldots)$, etc., will show any qualitatively different characteristics. For definiteness we consider the triplet states with symmetric spin functions: one could equally well consider the corresponding singlet states.

For purposes of calculating transition probabilities, the eigenfunctions of the states $(2p\sigma_u)\ (2s\sigma_g)\ C_u$ and $(2p\sigma_u)(2p\pi_u)\ B_g$ will be described by LCAO wave functions (i.e., combinations of one-electron hydrogen atom wave functions). If $a_\lambda(i)$, $b_\lambda(i)$ are (real) atomic orbitals of electron i $(i = 1,2)$ in the state $\lambda = 1s, 2s, 2px$ about nucleus A,B respectively, then our final state eigenfunctions are

$$(8a)\quad \Psi_{Bg} = N_{Bg}\Big[\Big\{a_{1s}(1) - b_{1s}(1)\Big\}\Big\{a_{2px}(2) - b_{2px}(2)\Big\} - \Big\{a_{2px}(1) - b_{2px}(1)\Big\}\Big\{a_{1s}(2) - b_{1s}(2)\Big\}\Big]$$

---

*cf. [5], p. 204, Fig.11.3. All that this says is that since the electronic energy of any bound H_2^+ state (i.e., the energy excluding the e^2/R term) is always negative, then if this energy is added to $E^{e\ell}(H_2^+\ 1s\ \sigma_g)$, the resulting curve cannot cross $E^{e\ell}(H_2{}^*\ 1s\sigma_g)$.

$$(9a)\ \Psi_{Cu} = N_{Cu}\left[\left\{a_{1s}(1) - b_{1s}(1)\right\}\left\{a_{2s}(2) + b_{2s}(2)\right\} - \left\{a_{2s}(1) + b_{2s}(1)\right\}\left\{a_{1s}(2) - b_{1s}(2)\right\}\right] .$$

The normalization constants N_{Bg}, N_{Cu} and the eigenfunctions are given in Apprendix B.

For the initial state, we shall describe the free incident electron by a plane wave referred to either one of the two nuclei:

$$(10)\ a_f(j) = (1/\sqrt{\Omega})\, e^{i(\underline{k}\cdot\underline{r}_{jA})} , \quad b_f(j) = (1/\sqrt{\Omega})\, e^{i(\underline{k}\cdot\underline{r}_{jB})} , \quad j = 1,2.$$

Strictly speaking, a_f, b_f should be continuous spectrum hydrogenic wave functions rather than plane waves. In constructing our total initial wave function, we note that symmetry with respect to inversion at the center of symmetry of AB -i.e.,the quantum number g or u - is still good. Thus we have two possible initial states:

$$(11a)\ \Psi_{Ig} = N_{Ig}\left[\left\{a_f(1) + b_f(1)\right\}\left\{a_{1s}(2) + b_{1s}(2)\right\} - \left\{a_{1s}(1) + b_{1s}(1)\right\}\left\{a_f(2) + b_f(2)\right\}\right],$$

$$(12a)\ \Psi_{Iu} = N_{Iu}\left[\left\{a_f(1) - b_f(1)\right\}\left\{a_{1s}(2) + b_{1s}(2)\right\} - \left\{a_{1s}(1) + b_{1s}(1)\right\}\left\{a_f(2) - b_f(2)\right\}\right] .$$

The normalization constants N_{Ig}, N_{Iu} are again listed in Appendix B.

Under the perturbation $V' = e^2/r_{12}$, even states go into even states, and odd into odd; thus we shall consider the two transitions

(13a) G: $Ig \rightarrow Bg$,

(13b) U: $Iu \rightarrow Cu$.

3. Results

Details of the calculation are sketched in Appendices C-F, but a summary will be presented here. Fig. 2 shows the values of wave number k from Eq. (3) that are required for the G- and U- transitions; we see that for values of the nuclear separation R that are frequently found for a molecular ion in its vibrational ground state the wave number k is fairly small, so that the transition matrix elements may be expanded in powers of k and all but the lowest-order terms neglected.

At low energies, the classical behavior of a reaction cross section as a function of k is

(14) $$\sigma = (b_o/k) + b_1 + b_2 k + \cdots .$$

This diverges for k = 0, but the physically relevant quantity is not the cross section but the transition probability per unit time, which is of order $\sigma k \sim b_o$, i.e., remains finite for zero energy. The cross section for the U-transition is given by the following expression:

(15) $$\begin{aligned} \sigma_U &= u_o(k_z^2/k^3) - u_1(k_z^4/k^3) + O(k^3) \\ u_0 &= 5.38 \times 10^{-17}\ \mathrm{cm}^2 \\ u_1 &= 6.30 \times 10^{-16}\ \mathrm{cm}^2 , \end{aligned}$$

where k is measured in units of a_o^{-1}, and the nuclear axis AB defines the z-axis. The value of u_1 has been calculated on the assumption

(16) $\underline{k}$ is parallel to $\underline{R}$ = AB, that is, $\underline{k} = (0,0,k)$.

The condition (16) was not used in deriving the value of u_o .

We see that the expansion breaks down for $ka_o > 0.292$, that is, for electron energies greater than 1.16 ev; however, we do see that the numerical value of the cross section is of the order of gas-kinetic cross sections (cf.Table I).

The G-transition is considerably more complicated. Let the orbital angular momentum define the x-direction, so that our final state is (1s, 2px) . Then if the two nuclei define the z-axis as before, and the electron wave number

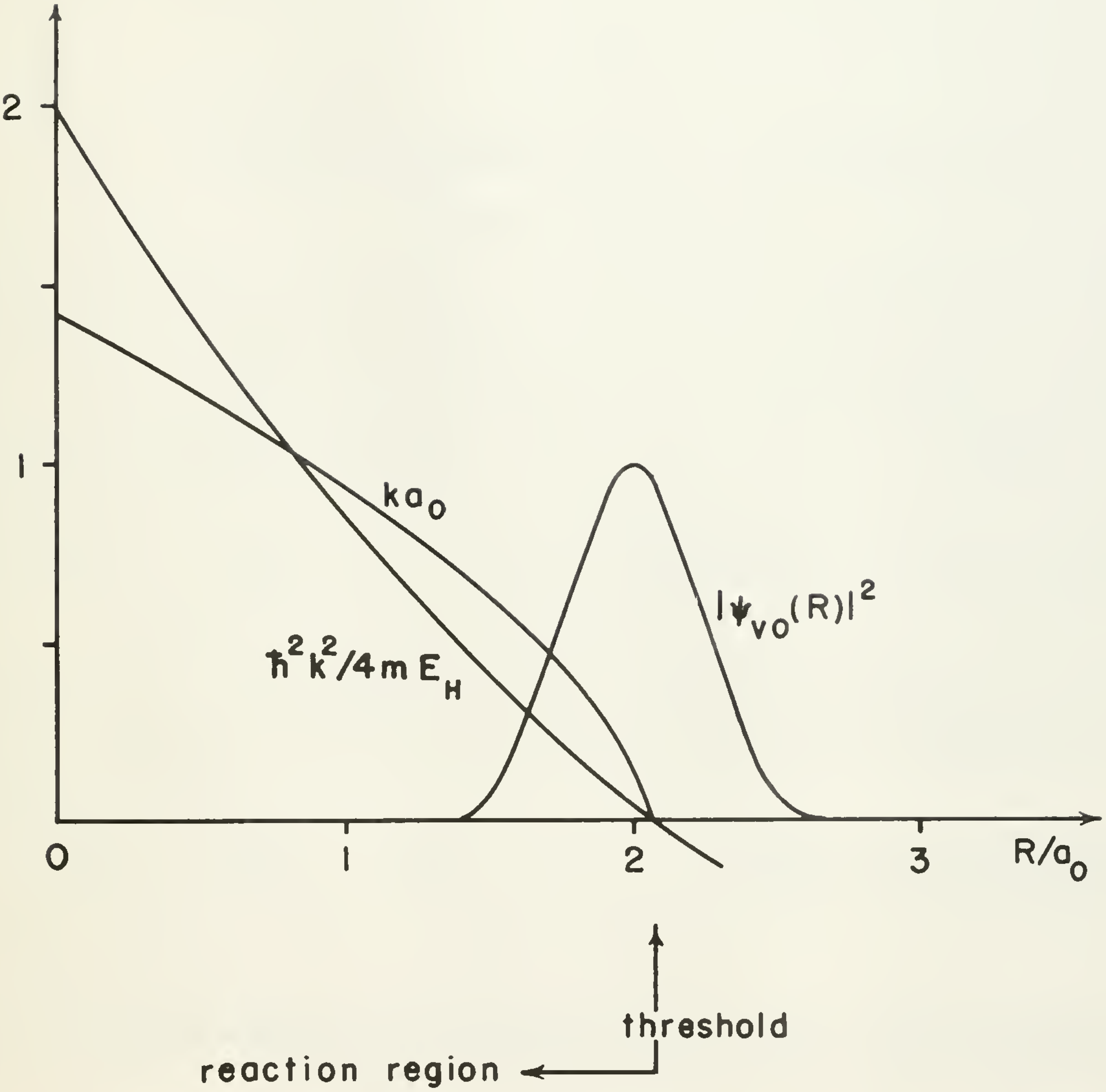

Figure 2

Electron wave number k and energy $h^2k^2/2m$ for the U- and G-transitions, as a function of nuclear separation R = AB. $|\Psi_{vo}(R)|^2$ is the relative probability of finding the molecular ion H_2^+ in its vibrational ground state at a given value of nuclear separation R.

Table I.

The cross section for G- and U-transitions in hydrogen as a function of energy.

Energy of incident electron	0	0.0258	0.10	1.16
wave number k,	0	0.04355	0.08575	0.292
σ_G, cross section for G-process,[*] 10^{-16} cm^2	0	7.9	15.5	53
σ_U, cross section for U-process,[**] 10^{-16} cm^2	∞	12.3	6.28	1.84
ratio $u_\perp k_z^2/u_o$ for U-process[†]	0	.022	.086	1.0

---

[*] calculated for electrons incident parallel to the molecular axis: $\underline{k} = (0,0,k)$

[**] calculated for electrons incident at an angle $\frac{\pi}{4}$ to the molecular axis: $\underline{k} = (k/\sqrt{2},\ 0,\ k/\sqrt{2})$

[†] Both σ_G and σ_U are calculated from the first term in Eqs. (17) and (15) respectively. The next term to σ_U is taken into account by multiplying σ_U by $(1-u_\perp k_z^2/u_o)$. It is thus clear that the last column, corresponding to an energy of 1.16 ev, is entirely unreliable.

$\underline{k} = (k_x, k_y, k_z)$ is again measured in units of a_0^{-1}, we find that

$$\text{(17)} \quad \begin{aligned} \sigma_G &= g_0(k_x^2 k_z^2 / k^3) + O(k^3) \\ g_0 &= 7.26 \times 10^{-14}\ \text{cm}^2 \ . \end{aligned}$$

Two striking features of this are, first, the absence of a $1/k$ term, so that the transition probability per unit time vanishes for zero energy. This arises directly from the cos ϕ term in the 2px wave function, i.e., from the existence of orbital angular momentum (cf. Appendix D). Second, the cross section would vanish if the electron were incident parallel to the nuclear axis. This is obvious classically, from the kind of impact needed to produce angular momentum about the x-direction.

One factor that ought to be considered is the effect of the nuclear vibration, which is discussed in Appendix E. It introduces certain complications into the definition of a reaction cross section, but does not change any quantitative results appreciably.

Quantitative results for the cross section as a function of energy are given in Table I for both G- and U-transitions; we see that both of these are of comparable importance.

One may ask whether any states other than those considered here will make an important contribution to the total capture cross section for dissociative recombination. We see from Fig. 1 that in the system H + H lower electronic states than the two considered here cannot be important; higher energy states are somewhat less favorable energetically than our two states, and thus would presumably lead to somewhat smaller contributions to the process. However, as a number of them have to be added, their net effect could well be significant. There is, however, no reason to suppose that the aggregate of all these states will lead to a total cross section very much larger than $5 - 10 \times 10^{-15}$ cm^2 .

Yet a further question relates to the possible application of these results to atoms other than hydrogen, such as helium or oxygen. Once again, one cannot be too definite without actually making the calculations, which are forbiddingly lengthy because of the large number of electrons involved. However, none of the arguments and calculations are specific in the sense that they depend on processes characteristic only to hydrogen and not to helium, etc.,[*] and thus it seems reasonable to infer from the present calculation that the total cross section for dissociative recombination for these other atomic species is again of gas kinetic order.

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[*] The quantum numbers and states involved are, of course, different for the different atoms, but the physical process does not involve these matters explicitly, but only insofar as conservation of energy and angular momentum are concerned.

Appendix A. Conservation of energy and momentum in capture processes

Consider a typical capture process

(A.1) $$A + B \longrightarrow C \ .$$

If the system C finishes with internal energy of excitation E_C', then the conditions of conservation of momentum, energy, and mass are

(A.2) $$m_A \underline{v}_A + m_B \underline{v}_B = m_C \underline{v}_C \ ,$$

(A.3) $$m_A v_A^2 + m_b v_B^2 = m_C v_C^2 + 2E_C' \ ,$$

(A.4) $$m_A + m_B = m_C \ .$$

Combining (A.2) (A.4), we get

(A.5) $$(\underline{v}_A - \underline{v}_B)^2 = 2 E_{C'} (m_A + m_B) / m_A m_B \ ,$$

which shows that in a capture process there must always be some relative kinetic energy

$$\frac{m_R}{2} v_R^2 \ ; \quad m_R = (m_A m_B) / (m_A + m_B) \ , \ \underline{v}_R = \underline{v}_A - \underline{v}_B$$

converted into internal energy of excitation* .

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*The case $\underline{v}_A = \underline{v}_B$, or $E_C' = 0$, does not correspond to a real collision, as A and B never meet in this case or else are always in contact.

Appendix B. Normalization of the wave functions

Following the convention [6], we shall use the following symbols for λ:

(B.1)
$$\left\{ \begin{array}{ccc} o & t & s \\ \updownarrow & \updownarrow & \updownarrow \\ 1s & 2s\sigma & 2px \end{array} \right. = \lambda \; .$$

Thus

(B.2a)
$$a_o(1) = \sqrt{(\alpha^3/\pi} \; e^{-\alpha r_{1A}}$$

(B.2b)
$$a_t(1) = \frac{\sqrt{(\alpha^3 2\pi)}}{2} \; (1 - \alpha r_{1A}/2 \; e^{-\alpha r_{1A}/2}$$

(B.2c)
$$a_s(1) = \frac{\sqrt{(\alpha^5/2\pi}}{4} \; r_{1A} e^{-\alpha r_{1A}/2} \; \sin(\theta_{1A}) \cos(\phi_{1A}) \; ,$$

and similarly for $b_{o,t,s}$.

Overlap integrals are defined as

(B.3)
$$I_{\lambda\mu} = (a_\lambda, b_\mu) = \int \alpha^3 \underline{r}_1 \; a_\lambda^* (1) \; b_\mu(1) \quad .$$

In particular, $I_{oo} = S$.

We now get the following results for the two final states:

(8b)
$$N_{Bg}{}^2 = 1/8 \left\{ 1 - I_{oo} - I_{ss} + I_{oo} . I_{ss} - \frac{(I_{os} + I_{so})^2}{4} \right]$$

(9b)
$$N_{Cu}{}^2 = 1/8 \left\{ 1 - I_{oo} + I_{tt} - I_{oo} . I_{tt} - \frac{(I_{ot} - I_{to})^2}{4} \right\}$$

Next, consider the initial states, which have to be looked at carefully on account of the continuous spectrum functions a_f, b_f of Eq. (10):

(10)
$$a_f(1) = (1/\sqrt{\Omega}\;) \; e^{i(\underline{k} \cdot \underline{r}_{1A})} \; , \text{ etc.,}$$

so that integration over the normalization volume Ω gives

(B.4a) $$(a_f, a_f) = (b_f, b_f) = 1$$

(B.4b) $$(a_f, b_f) = e^{i(\underline{k}\cdot\underline{r}_{AB})} = e^{-i(\underline{k}\cdot\underline{R})}$$

(B.4c) $$(b_f, a_f) = e^{i(\underline{k}\cdot\underline{R})}$$

The normalization volume Ω is chosen so large that for any bound state $\emptyset$

(B.5) $$(\emptyset,\emptyset) = 1,\ (a_f^*, \emptyset) \sim 1/\sqrt{\Omega} \longrightarrow 0\ ,\ (b_f^*, \emptyset) \sim 1/\sqrt{\Omega} \longrightarrow 0\ ,$$

so that cross products between free and bound states may be disregarded.

The normalization constants for the states Ig, Iu are given by

(11b) $$N_{Ig}^{\ 2} = 1/8\ (1 + I_{oo}) \left\{ 1 + \cos(\underline{k}\cdot\underline{R}) \right\}$$

(12b) $$N_{Iu}^{\ 2} = 1/8\ (1 + I_{oo}) \left\{ 1 - \cos(\underline{k}\cdot\underline{R}) \right\}\ .$$

Appendix C. Transition matrix element for the U-transition

The actual evaluation of the matrix elements is rather lengthy, and we shall introduce some additional notation, namely g- or u-orbitals denoted by ($\pm$):

(C.1) $$\emptyset_\lambda^{\pm}(i) = a_\lambda(i) \pm b_\lambda(i);$$

$$\lambda = 0(1s);\ \ t(2s);\ \ s(2p\pi_x);\ \ f(\text{plane wave - Eq. (10)}),$$

and also a real free-particle wave function labeled by the index $\lambda = k$:

(C.2) $$a_k(j) = (1/\sqrt{\Omega})\cos(\underline{k}\cdot\underline{r}_{jA})$$
$$b_k(j) = (1/\sqrt{\Omega})\cos(\underline{k}\cdot\underline{r}_{jB})\ .$$

Using (7), (9a), (12a) and (C.1), the transition matrix element now becomes

(C.3)
$$\frac{(\Psi_{Cu}, V'\Psi_{Iu})}{N_{Cu}N_{Iu}} = \Big(\phi_o^-(1)\phi_t^+(2) - \phi_t^+(1)\phi_o^-(2)\, V'\, \phi_f^-(1)\phi_o^+(2) - \phi_o^+(1)\phi_f^-(2)\Big)$$
$$= 2(\phi_o^-\phi_f^-\ V'\ \phi_o^+\phi_t^+) - 2(\phi_o^+\phi_o^-\ V'\ \phi_t^+\phi_f^-)\ ,$$

where we have written

(C.4)
$$(\phi_\lambda\phi_\mu\ V'\phi_\nu\phi_\rho) = \iint dv_1\ dv_2\ \phi_\lambda(1)\ \phi_\mu(1)\ V'(1,2)\ \phi_\nu(2)\ \phi_\rho(2)$$
$$= (\phi_\nu\phi_\rho\ V'\phi_\lambda\phi_\mu) \qquad \text{(no conjugate!)}$$

to indicate a convention we shall use: the wave functions in a matrix element that come to the left of V' $\left[V'(1,2) = e^2/r_{12}\right]$ are to be interpreted as functions of a variable $\underline{r}_1$, and those to the right as functions of $\underline{r}_2$.

A useful minor simplification may be achieved by noting that

(C.5)
$$\phi_o^+(1)\phi_o^-(1) = a_o(1)a_o(1) - b_o(1)b_o(1).$$

Further, note that the individual terms in the matrix element depend on two vectors, namely $\underline{R} = \underline{AB}$, and $\underline{k}$; interchanging the signs of both $\underline{R}$ and $\underline{k}$ simultaneously must leave the integrals invariant; that is, since only ϕ_f contains complex terms, interchanging A- and B-terms in the integrals and simultaneously taking the complex conjugate (i.e., changing the sign of $\underline{k}$) must leave the integrals invariant :

(C.6)
$$V(a,b,\underline{k}) = V(b,a,\underline{k})^* \qquad \text{for all V-terms.}$$

Applying the operations (C.5), (C.6) to (C.3), we find that

$$\text{(C.7)} \qquad \frac{(\Psi_{Cu}\ V'\Psi_{Iu})}{4N_{Cu}\ N_{Iu}} = (a_o\ \phi_t\ V'\phi_o\phi_k) + (b_o b_o\ V'\phi_t\phi_k)\ .$$

Notice that the use of (C.5), (C.6) has reduced the number of terms in the matrix element; the inherent symmetry in the centers A and B is now no longer exhibited, and also the transformation has led to the introduction of the real terms ϕ_k which came from $(\phi_f + \phi_f^*)/2$.

The next step is the evaluation of the terms of (C.7), and here several approximations will be made. The first integral will be approximated as follows:*

$$\text{(C.8)} \quad (a_o\phi_t^+ V'\phi_o^-\ \phi_k^-) = (a_o\overline{a_t+b_t}\ V'\phi_o^-\phi_k^-) \simeq (1 + I_{tt})(a_o a_t V'\phi_o^-\phi_k^-); \quad I_{tt} = (a_t, b_t).$$

In working out the various integrals it is convenient to use elliptic coordinates referred to A, B as foci, so that our coordinates are:

$$\text{(C.9)} \quad \begin{aligned} &\xi,\ \eta,\ \phi\ ;\ 1 < \xi < \infty,\ -1 < \xi < \infty,\ -1 < \eta < 1,\ 0 < \phi < 2\pi \\ &dv = (R^3/8)\,(\xi^2 - \eta^2)\ d\xi\, d\eta\, d\phi \\ &r_{1A} = (R/2)\,(\xi + \eta)\ ; \quad r_{1B} = (R/2)\,(\xi - \eta) \\ &(\underline{k}\cdot\underline{r}) = (k_x \cos\phi + k_y \sin\phi)(R/2)\sqrt{(\xi^2-1)(1-\eta^2)} + k_z R\,\xi\,\eta/2. \end{aligned}$$

We shall expand our matrix elements in powers of $\underline{k}$, retaining only the lowest-order terms. This simplifies things a great deal; the expansion gives

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* This is to be regarded as a plausible technical simplification, which should not introduce a large error.

$$\int dv\, f(\xi,\eta)\sin(\underline{k}\cdot\underline{r}) = \frac{k_z R}{2}\int d\xi d\eta\, f(\xi,\eta)\xi\eta(R^3/8)\,(2\pi)(\xi^2-\eta^2)$$

$$+\int dv\, f(\xi,\eta)\,(\underline{k}\cdot\underline{r})^3+\dots \qquad \text{(C.10)}$$

because the integration over the azimuth $\emptyset$ eliminates the troublesome k_x- and k_y-terms in the lowest-order term.

The effect of the k_x and k_y terms in general is to lead to Bessel functions

$$J_o\left(\frac{k_x R}{2}\sqrt{(\xi^2-1)(1-\eta^2)}\right)$$

which would be very tedious to evaluate. In any higher-order terms we shall attempt to investigate, these terms will be removed by the additional assumption

(16) $\underline{k}$ is parallel to $R = \underline{AB}$.

Note, however, that the assumption (16) is not necessary in the first order. We shall see in Appendix D that this assumption if used for lowest-order terms would make the cross section for the G-transition be identically zero.

Appendix D. Matrix element for the G-transition

By proceeding exactly as in the transformation from (C.3) to (C.7), we get the result

$$\frac{(\Psi_{Bg}V'\Psi_{Ig})}{4N_{Bg}\,N_{Ig}} = (a_s\emptyset_o^+V'\emptyset_o^-\,\emptyset_k^+) + (b_ob_oV'\emptyset_s^-\,\emptyset_k^+)\ . \qquad \text{(D.1)}$$

We shall now show that if we expand the integral in (D.1) in powers of $\underline{k}$, the lowest non-vanishing term is that of second order. Explicitly, we shall show that (D.1) vanishes for $\underline{k} = 0$; since the k-dependence introduced by $\emptyset_k$ is of type $\cos(\underline{k}\cdot\underline{r})$, this indicates that there can be no term of order lower than k^2, and in fact there is no reason to suppose that the k^2-term vanishes.

Let us first look at the second integral of (D.1). For $\underline{k} = 0$, we have

$$(D.2) \qquad (b_o b_o V'\phi_s^-) = \int dv_1 \phi_s^-(1) \int dv_2 \frac{[b_o(2)]^2}{r_{12}} = \int dv_1 \phi_s^-(1) f(r_{1B}) \ .$$

Now, $\phi_s(1)$ depends on r_{1A}, r_{1B}, ϕ_{1A}, ϕ_{1B}, and on $\phi_1 = \phi_{1A} = \phi_{1B}$. Transforming to elliptic coordinates (ξ, η, ϕ) we find that the only occurrence of the azimuth ϕ in (D.2) is in the $\phi_s(1)$-term, as $\cos(\phi)$. Thus, the identity

$$(D.3) \qquad \int_0^{2\pi} d\phi \cos(\phi) = 0.$$

shows that (D.2) vanishes. As a corollary, we can see that if $\underline{k} \neq 0$, and if (16) is satisfied, so that $\underline{k}$ is parallel to the line AB joining the two nuclei, then the matrix element $(b_o b_o V'\phi_s^-\phi_k^+)$ is identically zero. The argument is precisely the same as above.

Now look at the first term of (D.1) for the case $\underline{k} = 0$. Split it up into two parts:

$$(D.4) \qquad (a_s\phi_o^+V'\phi_o^-) = (a_s\phi_o^+V'a_o) - (a_s\phi_o^+V'b_o) \ .$$

Precisely as above, we can show that both parts vanish separately on account of the condition (D.3). We have

$$\begin{aligned}(a_s\phi_o V'a_o) &= \int dv_1 a_s(1)\phi_o^+(1) \int dv_2 a_o(2) / r_{12} \\ &= \int dv_1 a_s(1) f(r_{1A}, r_{1B}) \\ &= \int dv_1 a_s(1) f(\xi, \eta) \\ &= \int dv_1 \, g(\xi, \eta)\cos(\phi_1) = 0,\end{aligned}$$

as before. We have not yet succeeded in proving a corollary analogous to the previous case, namely that even higher-order terms in $\underline{k}$ will vanish if the condition (16) is satisfied. However, this seems rather plausible on physical grounds: the $\cos(\phi)$-term indicates that orbital angular momentum about the AB-axis has to be excited by the incident electron, but this is clearly impossible if the momentum $\underline{k}$ of the incident electron is wholly along the AB-axis.

Appendix E. Definition of a capture cross section

Consider the following problem. We have a beam of particles of definite energy E and direction $\underline{k}$, of intensity I_o, falling on the scatterer. The initial wave function of the system (incident particle plus scattering center) is Ψ_k, which is of course a continuous spectrum function. The final wave function is Ψ_β, corresponding to a bound state. We now ask - what is the cross section of the capture process?

Suppose we start with our initial continuous spectrum wave function normalized within a large volume Ω. Then the incident intensity $I_o = v/\Omega = hk/m\Omega$; the transition probability per unit time for the inverse process, i.e., from the bound state β to the free state $\underline{k}$, is

$$(E.1) \qquad P_{\beta k} = (2\pi/\hbar) \left|(\Psi_k, V'\Psi_\beta)\right|^2 \rho_E ,$$

where ρ_E is the number of final states $\underline{k}$ per unit energy range about the correct energy E. Thus, for an element $d\omega$ of solid angle, (E.2) $$\rho_E = \frac{m^2 v \Omega}{(2\pi\hbar)^3} \, d\omega ,$$

while in Born approximation the continuous spectrum wave function Ψ_k is *

(E.3) $$\Psi_k = (1/\sqrt{\Omega}\,) \, e^{i(\underline{k}\cdot\underline{r})} .$$

Combining (E.1)- (E.3), we get the result

(E.4) $$P_{\beta k} = (m/2\pi\hbar^2)^2 \, v \left| (\Psi_\beta, V \, e^{i(\underline{k}\cdot\underline{r})}) \right|^2 d\omega$$

for the decay probability per unit time.

If we now want the capture probability $P_{k\beta}$, we calculate it by dividing (E.4) by the number of initial states,

$$(4\pi p^3 \Omega) \,/\, (3\hbar^3) ,$$

over which we have integrated the decay probability in obtaining the result (E.4). The result is now

(F.5) $$P_{k\beta} = (m/2\pi\hbar^2)^2 \, v \left| (\Psi_\beta, V' e^{i(\underline{k}\cdot\underline{r})}) \right|^2 d\omega \, (3\hbar^3)/(4\pi p^3 \Omega).$$

Finally, the total capture cross section is

(E.6) $$\sigma_{k\beta} = P_{k\beta} \,/\, I_o = (m/2\pi\hbar^2)^2 \left| (\Psi_\beta, V' e^{i(\underline{k}\cdot\underline{r})}) \right|^2 (3/k^3) .$$

In applying this theory to our present problem, we have to consider the effect of the nuclear vibrational motion. In the previous discussion, as in Fig. 1,

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* If the scatterer has internal degrees of freedom, Ψ_k of (E.3) is replaced by $(1/\sqrt{\Omega}\,) e^{i(\underline{k}\cdot\underline{r})} \phi_{\text{internal}}$. For a normalized bound state ϕ_{internal} no problems arise.

we have treated the nuclei as existing at an arbitrary fixed separation R, and this has entered our calculations as a parameter. We now ask, for a molecular ion in its vibrational ground state, what is the probability of finding our two nuclei a given distance R to (R + dR) apart?

This probability is simply

$$\left|\Psi_{vo}(R)\right|^2 dR = \sqrt{(\beta/\pi)}\, \exp\left[-\beta(R-R_I)^2\right] dR; \quad \beta = M_I\, \omega_I/\hbar, \tag{E.7}$$

where R_I is the equilibrium nuclear separation of the ion, M_I ($= M_H/2$) is the reduced mass, and ω_I is the angular frequency of vibration.

From Fig. 2, we see that for small electron energies E_k the relation between E_k and the nuclear separation R is approximately linear; for $R < R_c$, which corresponds to zero kinetic energy, we have

$$R = R_c - K E_k \; ; \qquad K = -\,\partial R/\partial E_k \, . \tag{E.8}$$

Thus, taking into account the probability of finding the molecular ion at an appropriate nuclear separation, the capture cross-section for incident electrons in a small energy range E_k to $(E_k + dE_k)$ is

$$\begin{aligned} \sigma_{\text{capture},k\beta}(E_k \rightarrow E_k+dE_k) &= \sigma_{k\beta}(E_k) \cdot \left|\Psi_{vo}(R)\right|^2 \, |dR| \\ &= \sigma_{k\beta}(E_k)\, \Psi_{vo}(R)|^2 \; K\, dE_k \\ &= \sigma_{k\beta}(E_k)\, \sqrt{(\beta/\pi)}\, \exp\left[-\beta(-K E_k+R_c-R_I)^2\right] K\, dE_k \, , \end{aligned} \tag{E.9}$$

where $\sigma_{k\beta}(E_k)$ is given by the expression (E.6).

Notice that the capture cross section is here defined relative to a small range dE_k of incident energies. The reason for this is that the nuclear separation

R is a continuous variable, so that it makes sense only to ask for the probability of finding our two nuclei within a small range dR about R, and hence from Fig. 1b the requisite electron energy will lie in a range dE_k about E_k.

Appendix F. Expansion of the cross section in powers of k

It is clear from Fig. 1b that the cross section for either the G- or the U-process will fall off very rapidly with increasing electron energy on account of the nuclear vibrational motion, which is so restricted that a value of R corresponding to $E_k \gtrsim 7$ ev is quite improbable. In addition to this it is well known[3] that sufficiently far above the threshold the cross section for almost any inelastic collision falls off with increasing energy of the incident particle. Thus it is both convenient and legitimate to expand the cross section in powers of k.

Let us look first at the U-transition. From Eq. (C.7), the un-normalized matrix element depends on k through $\emptyset_k^-$, i.e., goes as $a_o k^2 + a_1 k^4 + \ldots$; now, recalling that

$$\text{(12b)} \qquad N_{Iu}{}^2 \sim 1/\left\{1 - \cos(\underline{k}\cdot\underline{R})\right\} \sim 1/(\underline{k}\cdot\underline{R})^2 \; ,$$

we find that

$$\text{(F.1)} \qquad (\Psi_{Cu}, V'\Psi_{Iu}) = c_o k + c_1 k^3 + \ldots \; .$$

Now consider the expressions (E.6), (E.9) for the cross section. From (E.6) we see that $\sigma_{k\beta} \sim |V'_{k\beta}|^2 (1/k^3)$; the exponential factor in (E.9) does not produce any significant effect at the lowest energies (cf. Fig. 1b), and so we have

(F.2) $$\sigma_{cap,U}(E_k \rightarrow E_k + dE_k) = (d_o/k + d_1k + \ldots)\, dE_k \, .$$

The 1/k-variation is just the classical one: the capture probability per unit time per unit energy range is just

$$\sigma_{cap} \times \text{velocity } (-hk/m) \Big/ dF_k = \frac{\hbar}{m}(d_o + d_1k^2 + \ldots),$$

and this capture probability remains finite at low energies, as it should.

If we now consider the G-transition, we see from Appendix D that the un-normalized matrix element again begins with a term in k^2. From (11b) we find that the normalizing factor $N_{Ig}^{\;2} \sim 1/\left\{1 + \cos(\underline{k}\cdot\underline{R})\right\} \sim 1$, so that the matrix element is

(F.3) $$(\Psi_{Bg}, V'\Psi_{Ig}) = e_ok^2 + e_1k^4 + \ldots \, ,$$

while by the same argument as before,

(F.4) $$\sigma_{cap,G}(E_k \rightarrow E_k + dE_k) = (f_ok + f_1k^3 + \ldots)\, dE_k \, .$$

This difference between the U- and G-transitions arises evidently from the fact that orbital angular momentum has to be excited in the G-transition; from the k-dependence it is thus clear that the U-transition will be the more important one in practice.

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